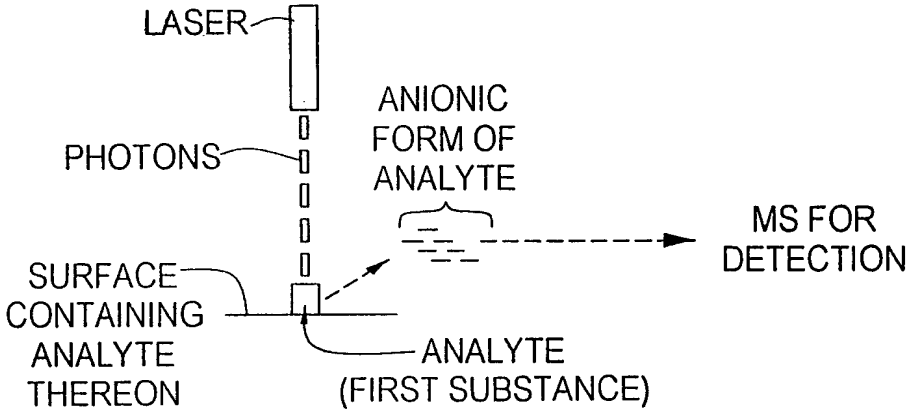
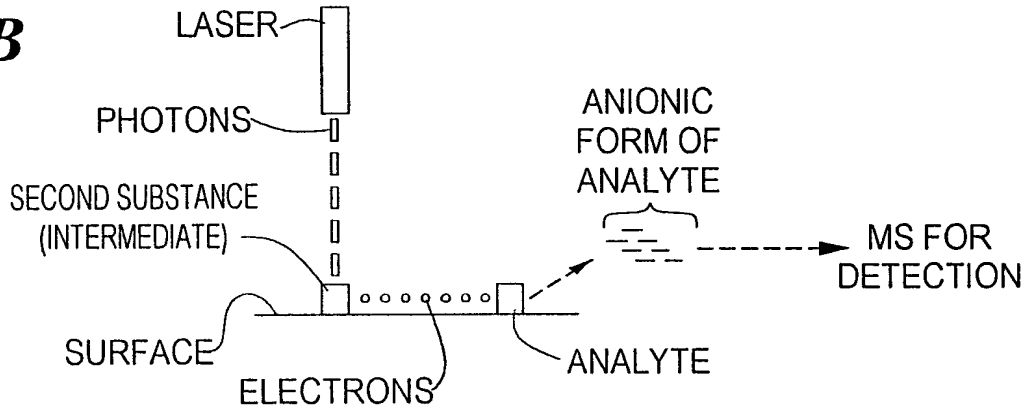
FIG. 1A



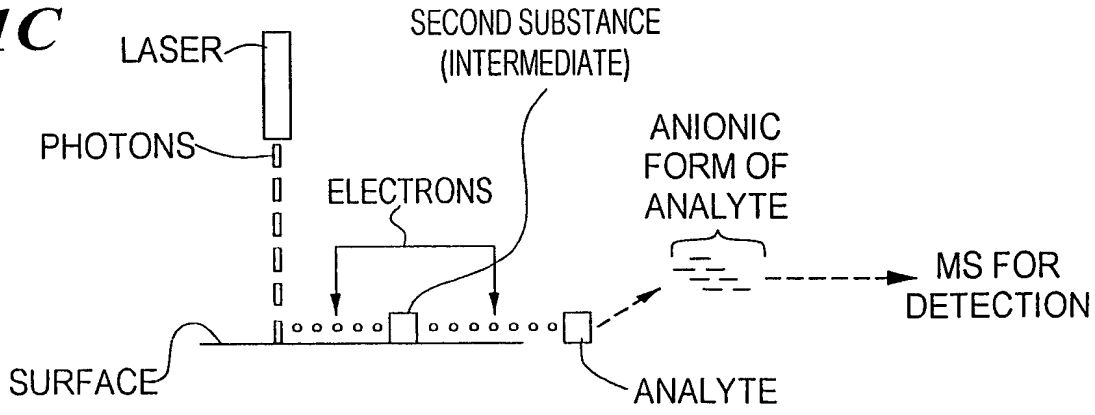
ELECTRONS FROM SURFACE TO ANALYTE

FIG. 1B



ELECTRONS FROM INTERMEDIATE TO ANALYTE

FIG. 1C



ELECTRONS FROM SURFACE TO INTERMEDIATE TO ANALYTE

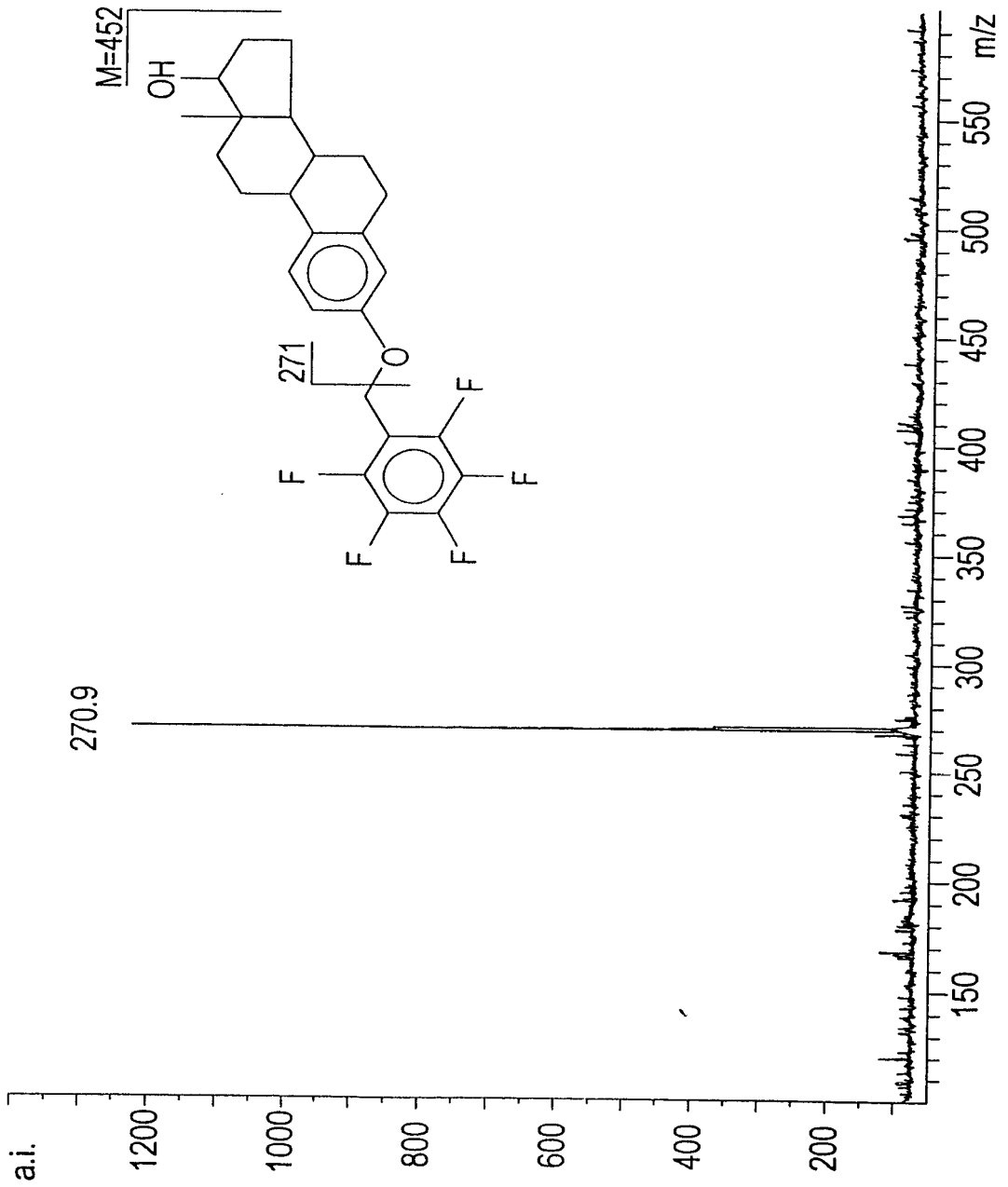

M=452
OH
271
O
F
F
F
F
F
270.9
a.i.
1200
1000
800
600
400
200
150
200
250
300
350
400
450
500
550
m/z

FIG. 2

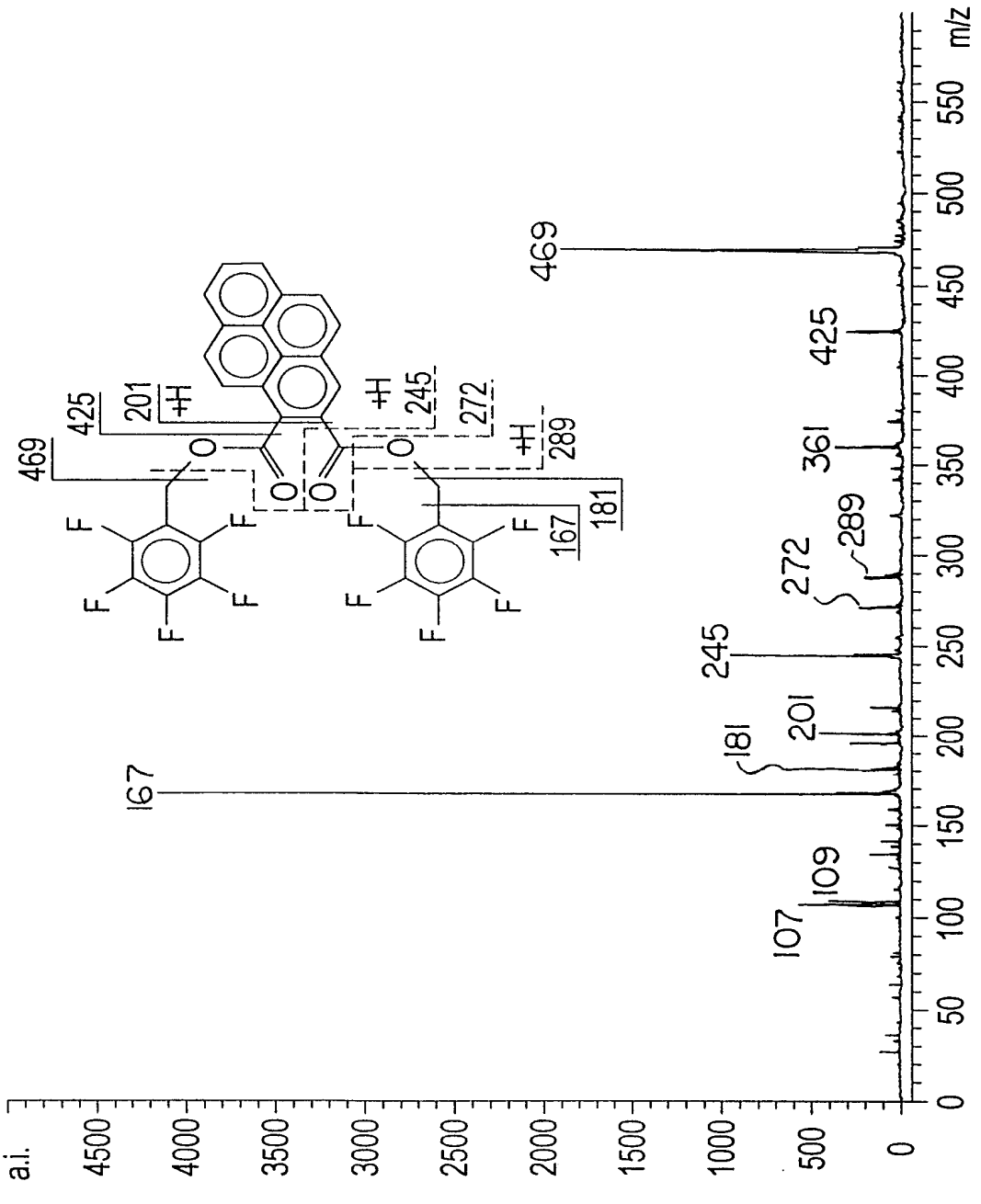

a.i.
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
50
100
150
200
250
300
350
400
450
500
550
m/z
469
425
361
289
272
245
201
181
167
109
107
F
O
+H

FIG. 3

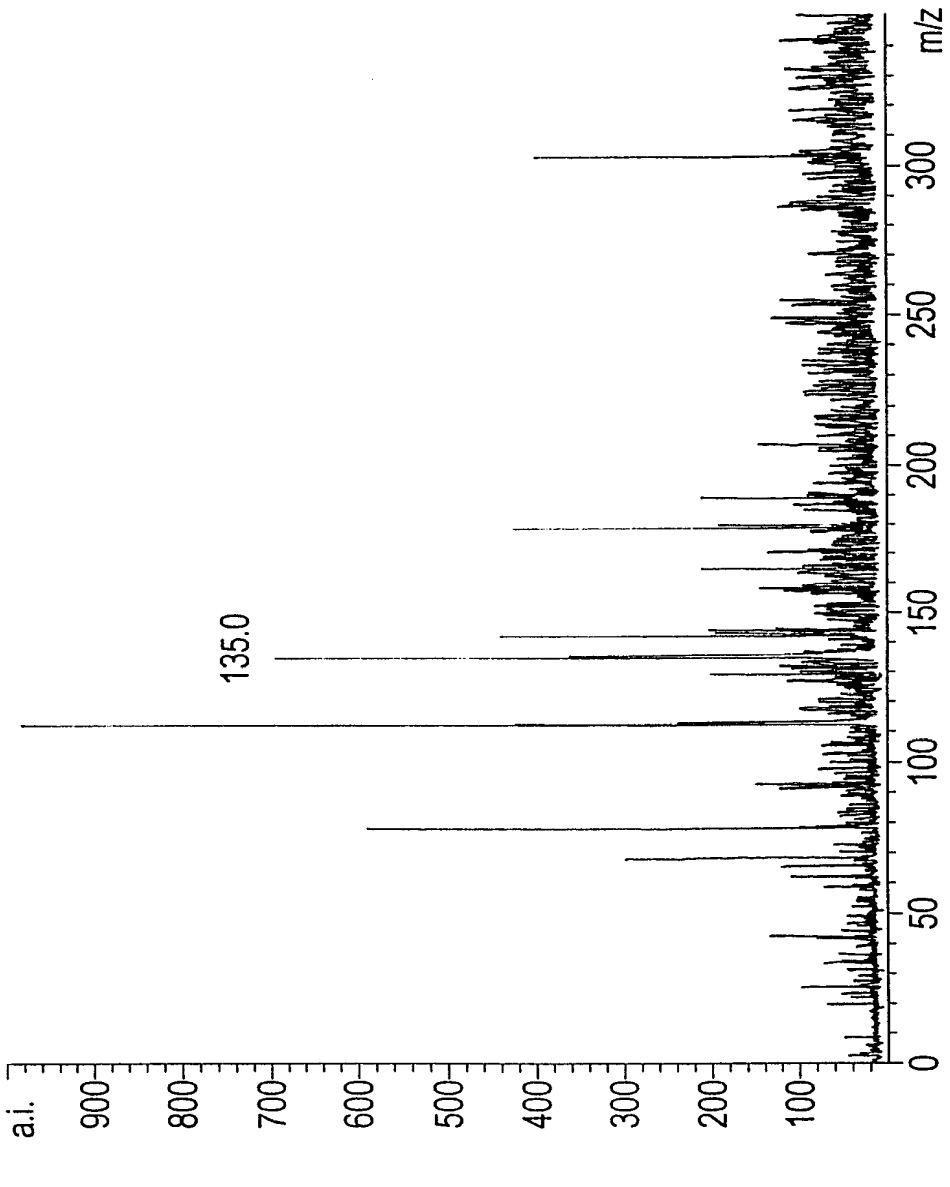

a.i.
900
800
700
600
500
400
300
200
100
0
50
100
150
200
250
300
m/z
135.0

FIG. 4A

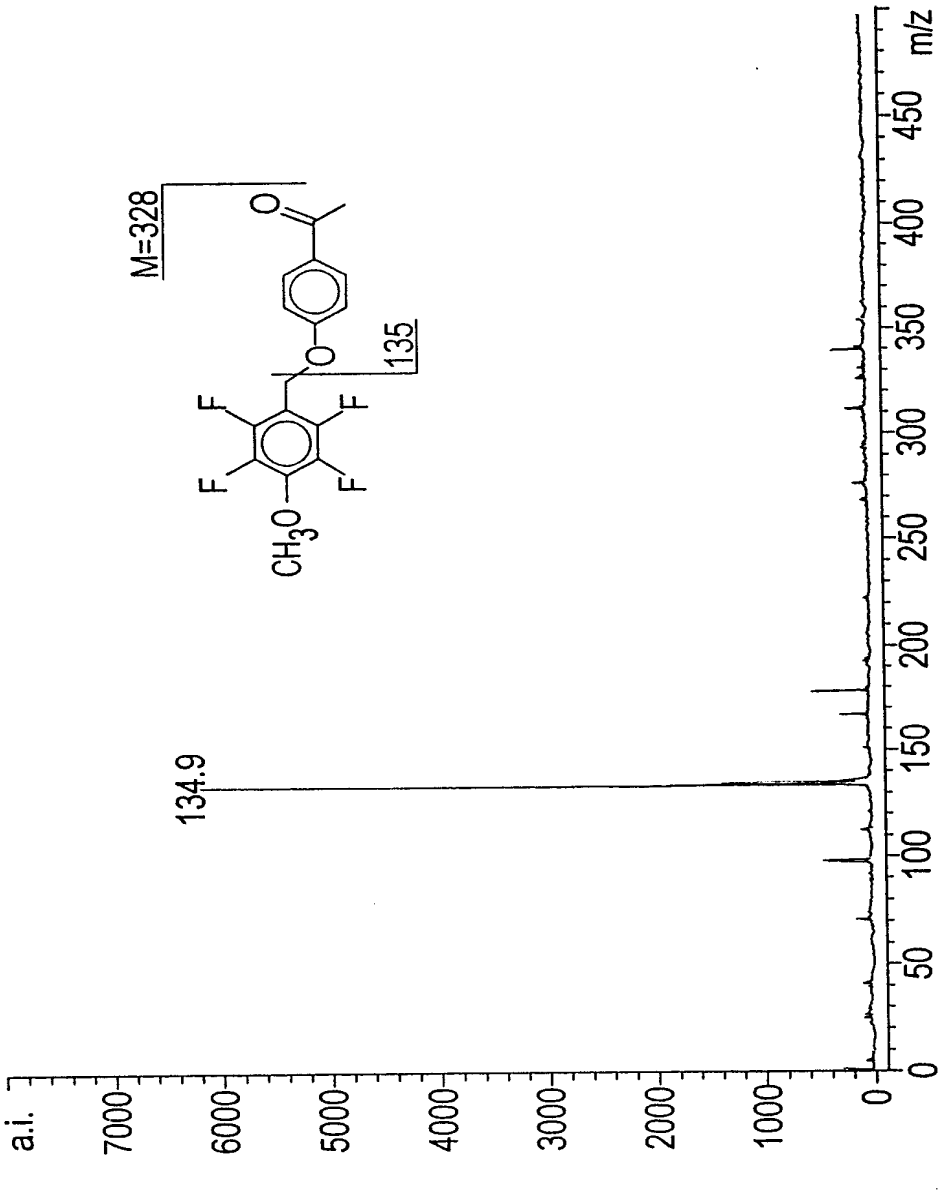

a.i.
7000
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
250
300
350
400
450
m/z
134.9
M=328
135
O
O
F
F
F
F
CH_3O

FIG. 4B

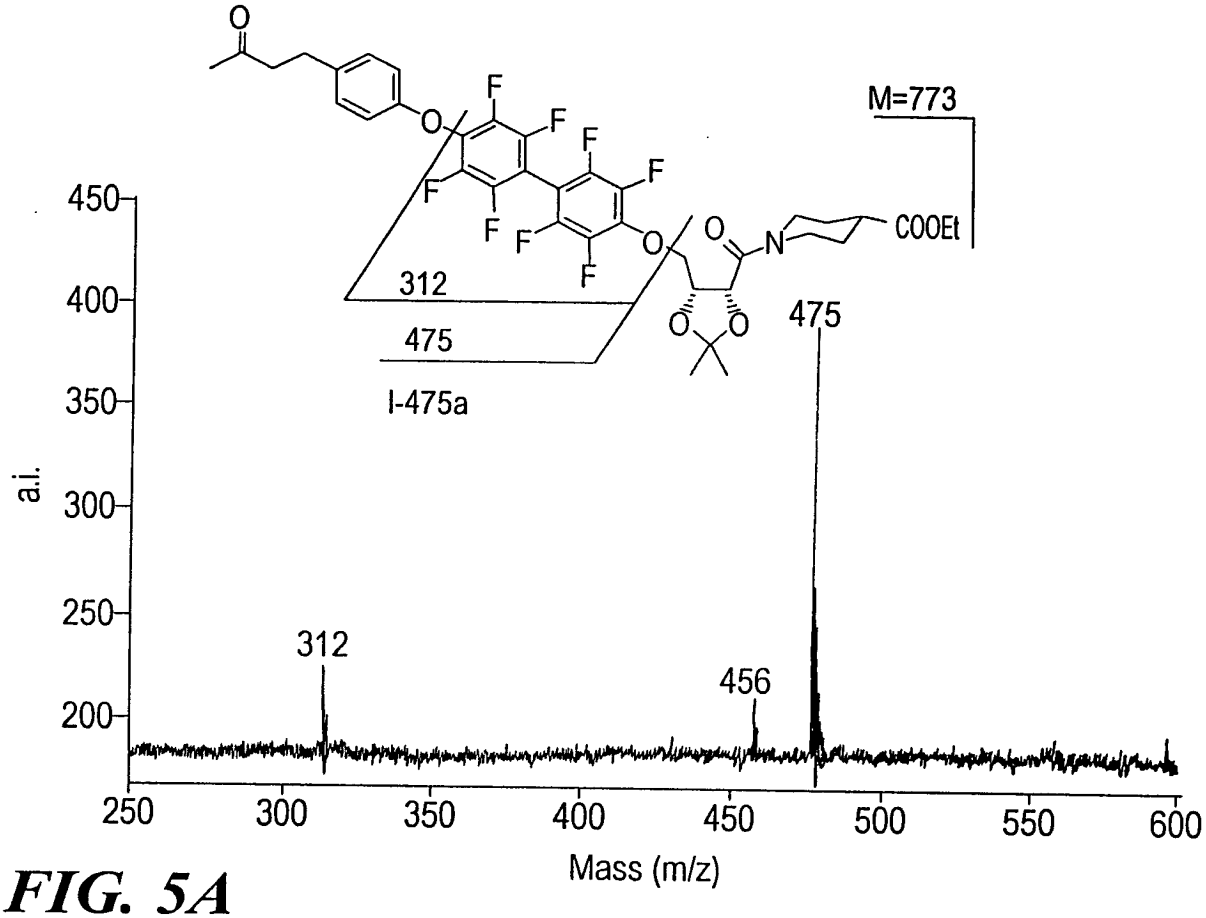

M=773
COOEt
312
475
I-475a
a.i.
450
400
350
300
250
200
312
456
475
250
300
350
400
450
500
550
600
Mass (m/z)

FIG. 5A

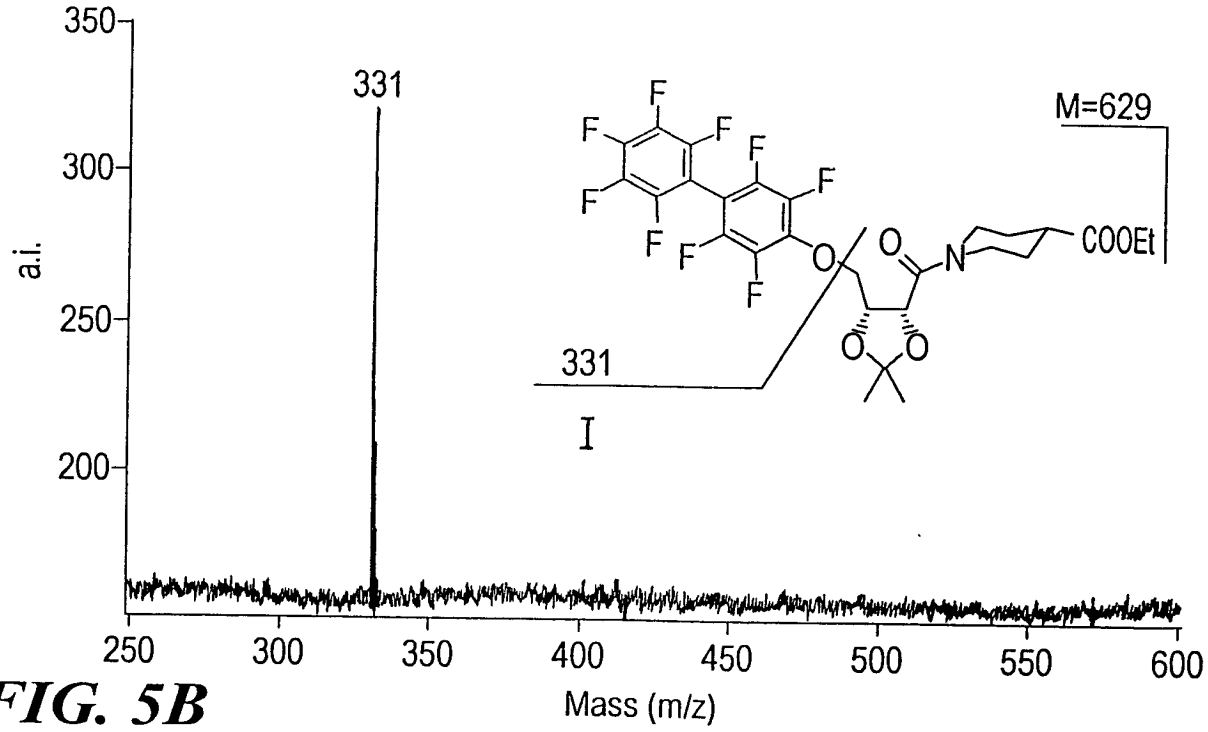

M=629
COOEt
331
I
a.i.
350
300
250
200
331
250
300
350
400
450
500
550
600
Mass (m/z)

FIG. 5B

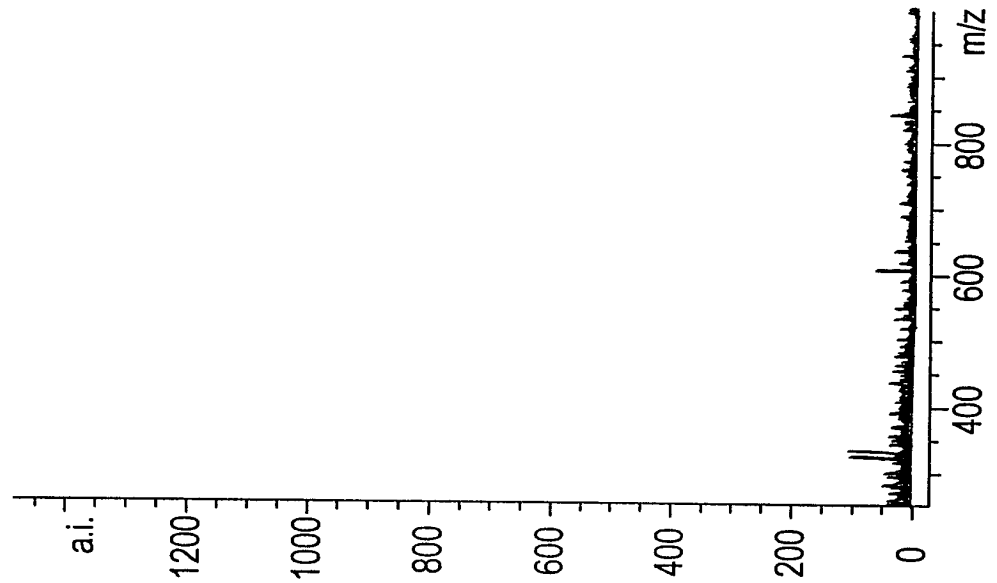

a.i.
1200
1000
800
600
400
200
0
400
600
800
m/z

FIG. 6B

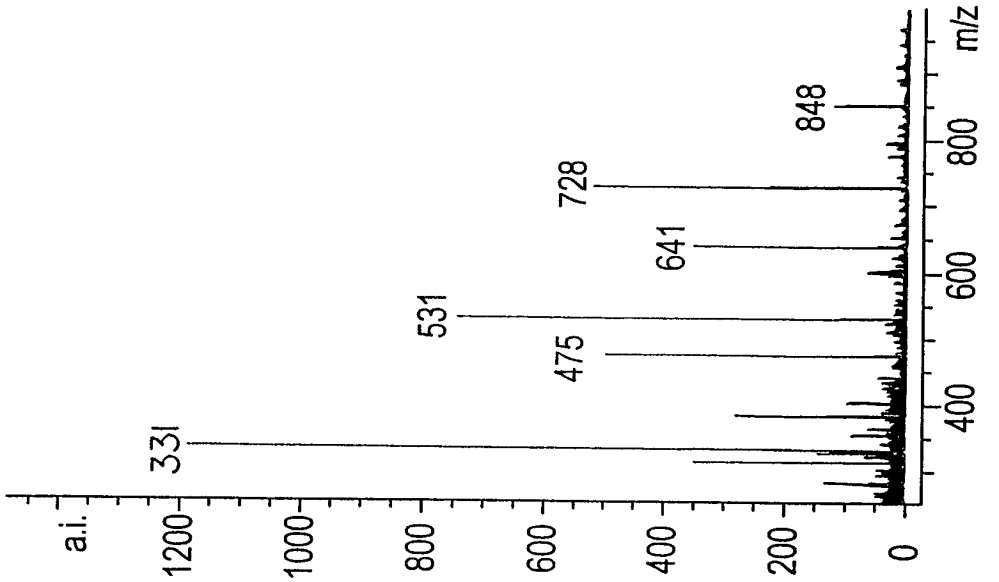

a.i.
1200
1000
800
600
400
200
0
331
475
531
641
728
848
400
600
800
m/z

FIG. 6A

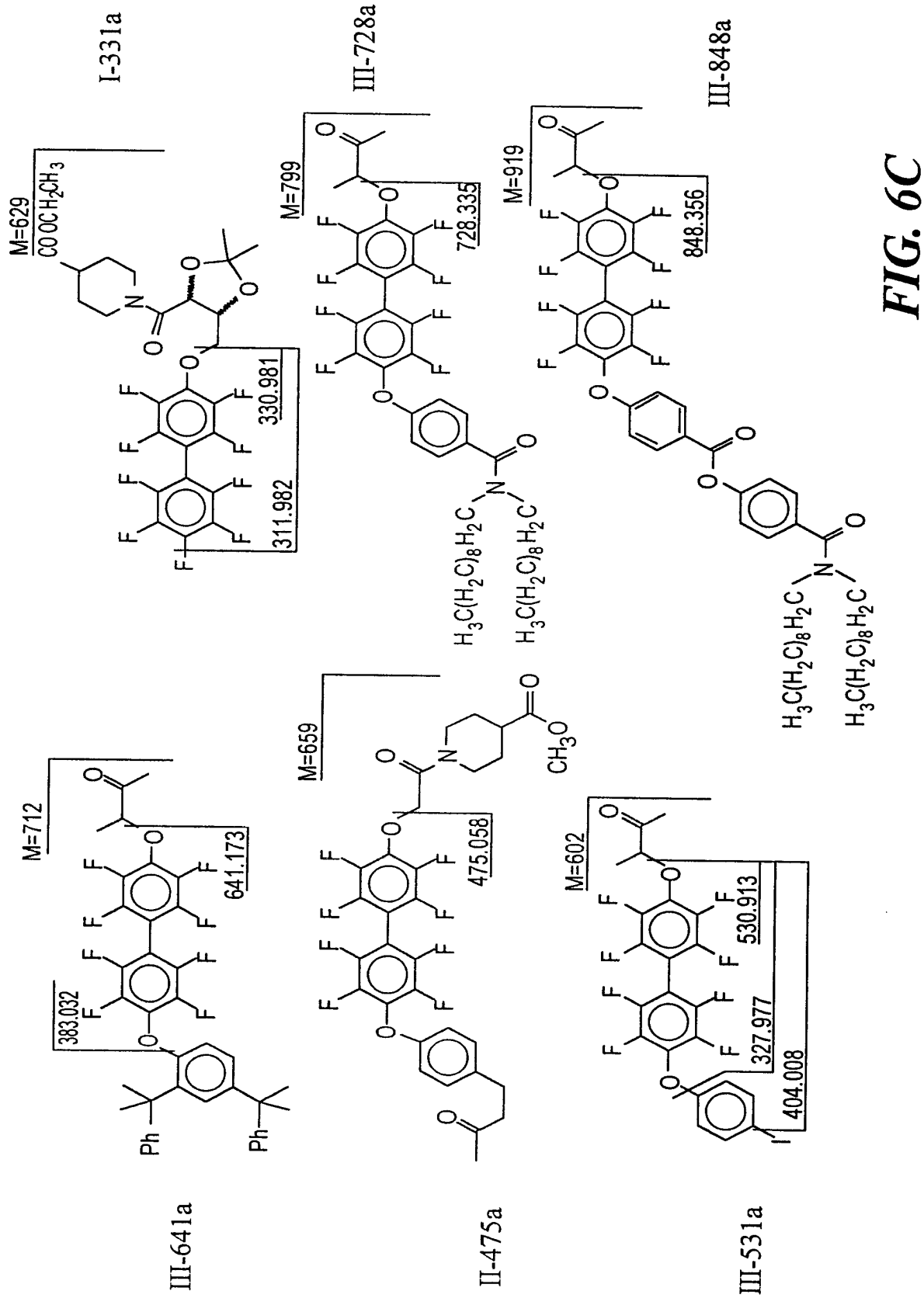

I-331a
M=629
330.981
311.982
III-728a
M=799
728.335
III-848a
M=919
848.356
III-641a
M=712
641.173
383.032
II-475a
M=659
475.058
III-531a
M=602
530.913
327.977
404.008

FIG. 6C

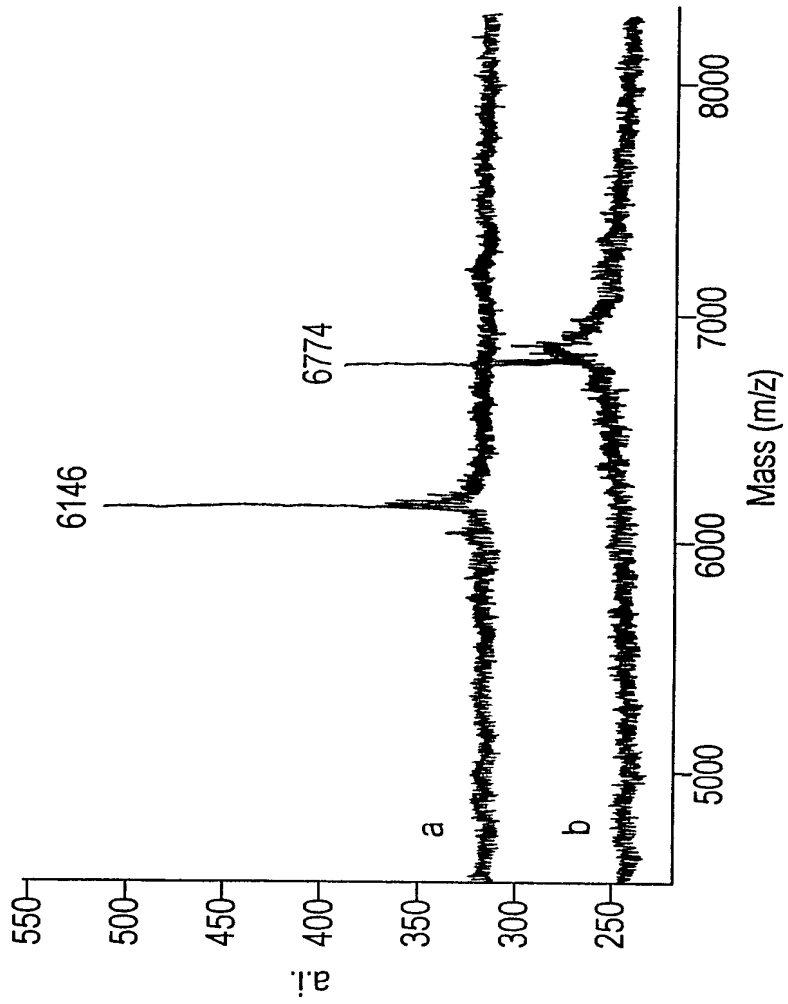

6146
6774
a
b
550
500
450
400
350
300
250
a.i.
5000
6000
7000
8000
Mass (m/z)

FIG. 7A

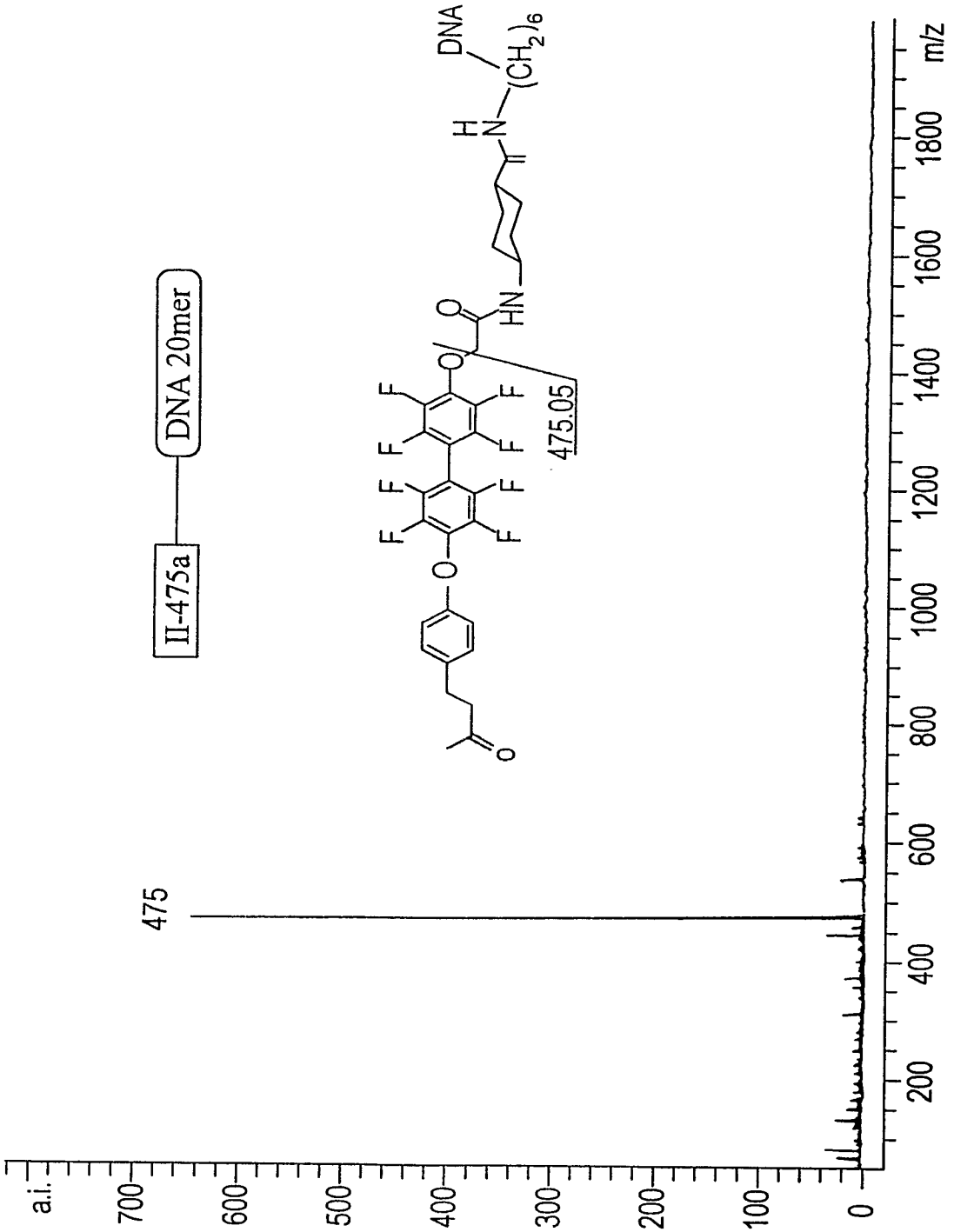

a.i.
700
600
500
400
300
200
100
0
200
400
600
800
1000
1200
1400
1600
1800
m/z
475
II-475a
DNA 20mer
475.05
DNA
$(CH_2)_6$
HN
O
F

FIG. 7B

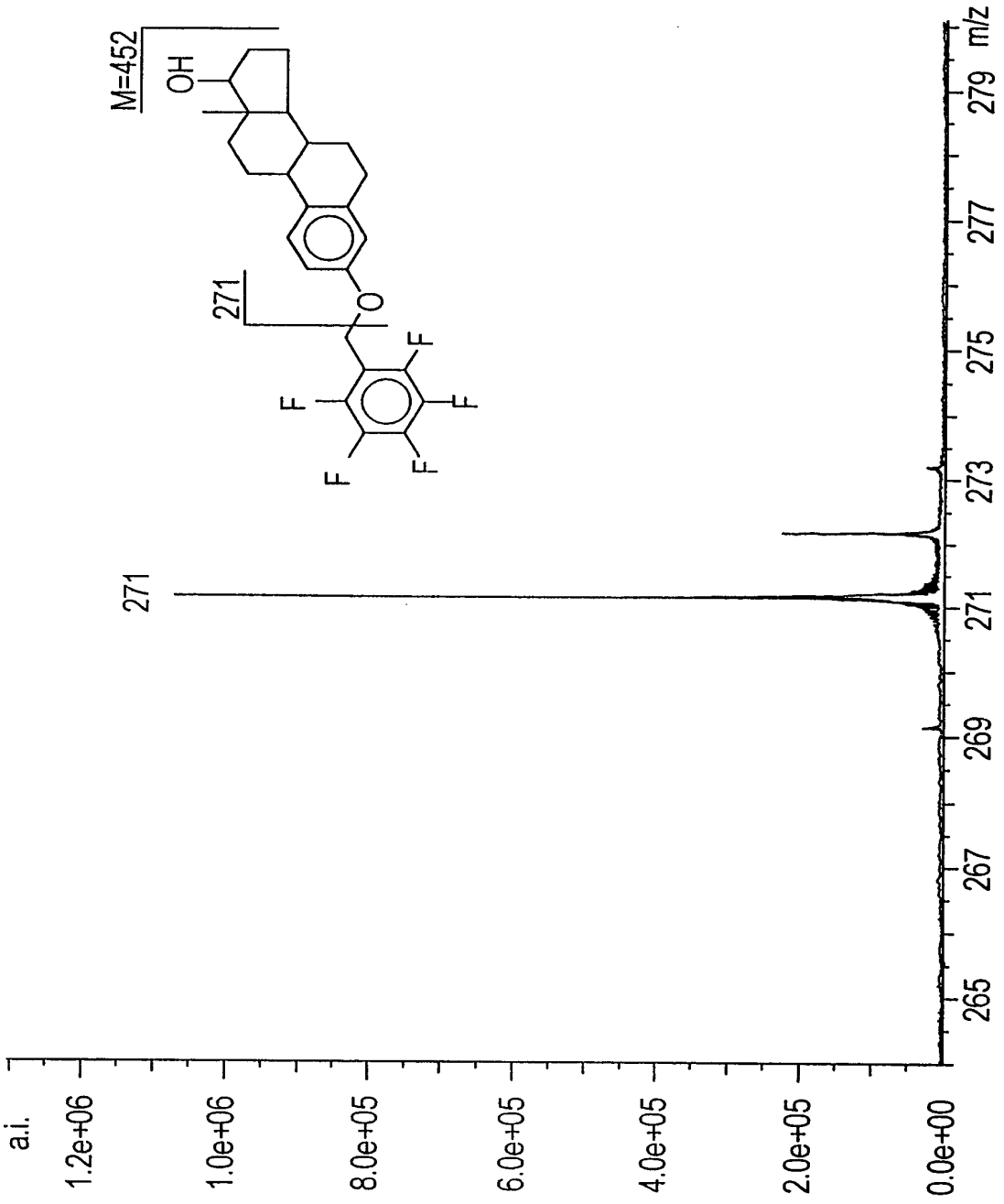

M=452
OH
271
O
F
F
F
F
271
a.i.
1.2e+06
1.0e+06
8.0e+05
6.0e+05
4.0e+05
2.0e+05
0.0e+00
265
267
269
271
273
275
277
279
m/z

FIG. 8

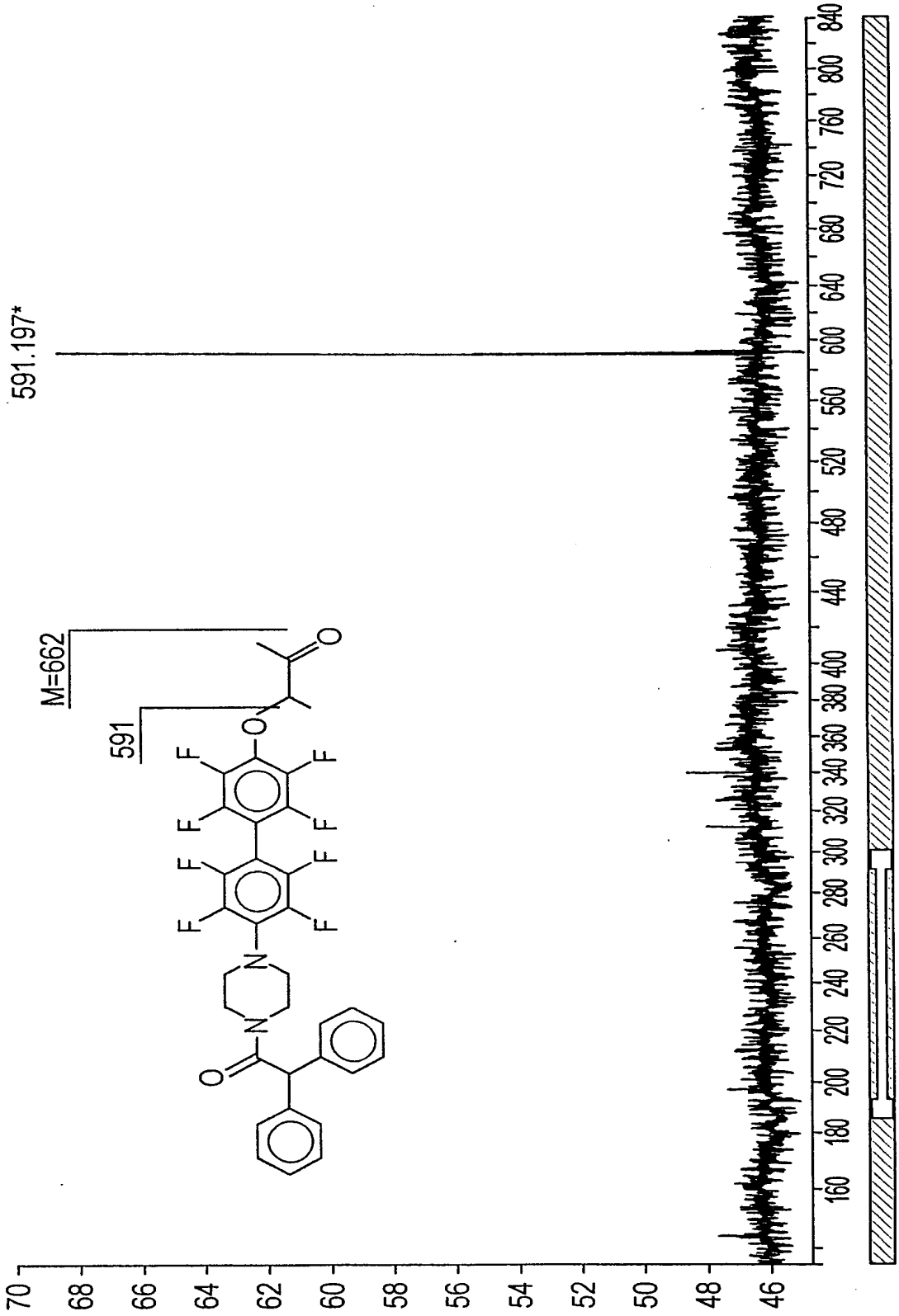

591.197*
M=662
591
O
F
N
O
70
68
66
64
62
60
58
56
54
52
50
48
46
160
180
200
220
240
260
280
300
320
340
360
380
400
440
480
520
560
600
640
680
720
760
800
840

FIG. 9